

# **$s$ - $d$ electronic interactions induced $H_2$ dissociation on the $\gamma$ -U(100) surface and influences of niobium doping**

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## **Abstract**

The dissociation of hydrogen molecules on the  $\gamma$ -U(100) surface is systematically studied with the density functional theory method. Through potential energy surface calculations, we find that hydrogen molecules can dissociate without any barriers on the clean  $\gamma$ -U(100) surface. After careful electronic analysis, it is found that charge transfer between the hydrogen  $s$  and uranium  $d$  electronic states causes the dissociation, which is quite different from the dissociation of hydrogen molecules on other actinide metal surfaces. Considering that doping of  $3d$  transition metal atoms can stabilize the  $\gamma$  phase of U, we also study the influences of Nb-doping on the hydrogen dissociation process. We find that the  $3d$  electronic states of Nb also take part in the hybridization with hydrogen  $s$  electronic states, which leads to the result that hydrogen molecules also dissociate without any energy barriers on the doped U surface. In addition, the free electronic energy lowers down more quickly for a hydrogen molecule approaching the doped U surface.

## I. INTRODUCTION

During the past decades, many theoretical and experimental studies have been carried out on the initial processes of surface hydrogenation or oxidation reactions<sup>1–17</sup>. The theoretical researches include calculating the potential energy surfaces for H<sub>2</sub> or O<sub>2</sub> molecules on solid surfaces, and revealing the adsorption and dissociation mechanisms of them<sup>6–17</sup>. In the experimental aspect, ultrahigh vacuum experiments are designed to detect the atomic structures after very few numbers of molecules reacting with solid surfaces<sup>3–5</sup>. Actinides, as a group of radioactive, toxic and rare materials<sup>18</sup>, have their difficulties to be prepared for such experimental studies. On the other hand, they play important roles in advanced nuclear fuel cycles, and surface hydrogenation/oxidation are the main corrosion mechanisms that fail their storage<sup>19–23</sup>. Hence, theoretical studies are crucial for understanding the detailed surface corrosion mechanisms in the presence of environmental gases for these high- $Z$  elements. Moreover, these studies may also help to address the environmental consequences of nuclear materials.

Among the actinide elements, uranium (U) is the heaviest naturally occurring one, which occupies a central position in the early actinide series<sup>18,24</sup>. Due to its important role in nuclear reactors, U is quite familiar to people<sup>18</sup>. In the atmosphere, U and its alloys are ready to be oxidized to form U oxide layers, which subsequently break down through a hydrogenation process. The hydriding reaction proceeds by surface nucleation and growth of hydride nuclei which spread over the sample surfaces<sup>25–27</sup>. It has been revealed that the hydride nuclei form beneath the oxide layers, and most of them are capable of penetrating through the oxide layers above them to grow over time until they consume the sample surface<sup>27,28</sup>. Based on these knowledges, one can see that the electronic interaction with hydrogen molecules is critically important for the corrosion of U surfaces. Pure uranium crystallizes into several structures, the orthorhombic  $\alpha$  phase with four molecules per unit cell at ambient conditions, followed by the body-centered tetragonal  $\beta$  (bct) phase at 940 K and then the body-centered cubic  $\gamma$  (bcc) phase at 1050 K at ambient pressure<sup>18,24,29–31</sup>. Moreover, the high temperature  $\gamma$  phase can be studied at normal temperatures by the addition of certain metals like molybdenum and niobium, which stabilizes the  $\gamma$  phase at room temperature and below<sup>18,29</sup>. In metallic U, the three  $5f$  electrons of U hybridize with the  $6d$  and  $7s$  electrons, and show itinerant behaviors<sup>18,24,32</sup>. Therefore, density functional

theories without any modifications concerning localized electronic states are appropriate within a large extent to describe metallic U.

Recently, many theoretical and computational studies emerge on the surface chemical properties of uranium and other actinide metal surfaces. Using the density functional semi-core pseudopotential method, the chemisorption of carbon monoxide<sup>18</sup> and oxygen gases<sup>24</sup> on the  $\gamma$ -U surfaces have been investigated focusing on the geometric, magnetic and electronic properties of the system. The adsorption of carbon monoxide on  $\alpha$ -U surfaces has also been studied using a plane-wave ultrasoft pseudopotential<sup>33</sup>. For the interaction between hydrogen and U, present theoretical studies are all carried out on the  $\alpha$ -U surfaces<sup>19,34,35</sup>. Different from the hydrogen dissociation on transition-metal surfaces, where electronic hybridizations between hydrogen  $1s$  electrons and surface  $d$  electrons induce the dissociation<sup>36</sup>, the dissociation of hydrogen molecules on the  $\alpha$ -U surface is because of  $5f$ - $1s$  hybridizations<sup>19</sup>, which is similar to the hydrogen dissociation on  $\delta$ -Pu surfaces<sup>37</sup>. Here in this paper, by using first-principles calculations, we systematically study the adsorption and dissociation processes of hydrogen molecules on the  $\gamma$ -U(100) surface, and reveal that the  $d$  electrons of U, instead of its  $f$  electrons, take part in the electronic hybridizations with hydrogen  $1s$  electrons. This result clearly presents different surface chemical properties of  $\alpha$ - and  $\gamma$ -U. Considering that the  $\gamma$  phase of U is available at normal temperatures only after doping with  $3d$  transition metals, here we also investigate the influences of surface Nb doping on the dissociation properties of hydrogen molecules.

## II. CALCULATION METHOD

Our calculations are performed within density functional theory using the spin-polarized edition of Vienna *ab initio* simulation package (VASP)<sup>38</sup>. The Perdew-Burke-Ernzerhof (PBE)<sup>39,40</sup> generalized gradient approximation and the projector-augmented wave potential<sup>41</sup> are employed to describe the exchange-correlation energy and the electron-ion interaction, respectively. The cutoff energy for the plane-wave expansion is set to 520 eV. The U(100) surface is modeled by a slab composing of five atomic layers and a vacuum region of larger than 15 Å. The bottom two layers are fixed, and the other U layers are free to move during the geometry optimizations of the uranium surfaces. A  $2 \times 2$  supercell, in which each monolayer contains four U atoms is adopted in the study of the  $H_2$  adsorption.

Our test calculations have shown that the  $2\times 2$  supercell is sufficiently large to avoid the interaction between adjacent  $\text{H}_2$  molecules. Integration over the Brillouin zone is done using the Monkhorst-Pack scheme<sup>42</sup> with  $5\times 5\times 1$  grid points. And a Fermi broadening<sup>43</sup> of 0.2 eV is chosen to smear the occupation of the bands around the Fermi energy  $E_F$  by a finite- $T$  Fermi function and extrapolating to  $T=0$  K. The  $\text{H}_2$  is placed on one side of the slab, namely, on the top surface. The calculation of the potential-energy surface is interpolated to 350 points with different bond length ( $d_{\text{H-H}}$ ) and height of the mass center ( $h_{\text{H}_2}$ ) of  $\text{H}_2$  at each surface site. The calculated lattice constant of  $\gamma\text{-U}$  and bond length of a free  $\text{H}_2$  molecule are 3.43 and 0.75 Å, respectively, in good agreement with the experimental values of 3.467<sup>18</sup> and 0.74 Å<sup>44</sup>.

### III. RESULTS AND DISCUSSION

#### A. Hydrogen dissociation on the clean $\gamma\text{-U}(100)$ surface

The geometry and electronic properties of the clean  $\gamma\text{-U}(100)$  surface is firstly investigated. After geometry optimization, we find that the two topmost U layers relax significantly from the bulk values. The first-second interlayer is contracted by 26.4% and the second-third interlayer is expanded by 15.6%. The huge surface relaxation reflects that the surface electronic structure should be quite different from that in the bulk. The projected density of states (PDOS) around the Fermi energies are then calculated for bulk U and the  $\gamma\text{-U}(100)$  surface, and shown in Fig. 1(a). We can see that in the PDOS for bulk U, the occupied electronic states are itinerant without any localized peaks, which is in good agreement with previous theoretical studies<sup>18,24</sup>. For the U atom in the  $\gamma\text{-U}(100)$  surface, the narrow peaks in the unoccupied  $f$  states disappear. This result supports the experimental observations in X-ray and ultraviolet photoelectron spectroscopy, and auger electron spectroscopy that localization effects are weak in U films<sup>32</sup>. The PDOS for an U atom in  $\alpha\text{-U}$  and in the  $\alpha\text{-U}(001)$  surface is also shown in Fig. 1(b). One can see that there are more  $f$  electrons for the U atom in the  $\alpha\text{-U}(001)$  surface than in  $\alpha\text{-U}$ , which corresponds to the charge transfer from bulk to the surface atomic layer. Comparatively, such kind of charge redistribution is not seen for the  $\gamma\text{-U}(100)$  surface.

After studying the geometry and electronic property of the  $\gamma\text{-U}(100)$  surface, we build our

models to calculate the two-dimensional (2D) potential energy surface (PES) cuts for  $\text{H}_2$  on the relaxed uranium surface. As shown in Fig. 2(a), there are three different high-symmetry sites on the clean U surface, respectively, the top, bridge (bri), and hollow (hol) sites. At the bridge site, an adsorbed  $\text{H}_2$  has three different high-symmetry orientations, respectively along the  $x$  (i.e.,  $[001]$ ),  $y$  (i.e.,  $[010]$ ), and  $z$  (i.e.,  $[100]$ ) directions. Nevertheless, at the top and hollow sites, the  $x$  and  $y$  directions are degenerate, and the three high-symmetry orientations become the  $x$ ,  $d$  (i.e.,  $[011]$ ), and  $z$  directions. Herein, we use top- $x, d, z$ , bri- $x, y, z$ , and hol- $x, d, z$  to represent the nine high-symmetry channels for the adsorption of  $\text{H}_2$  on the  $\gamma\text{-U}(100)$  surface, respectively. We have also constructed several low-symmetry initial structures by rotating the  $\text{H}_2$  molecule in the  $XY$ ,  $YZ$ , and  $XZ$  planes with small angles. Through PES calculations, we find that the energy barrier for  $\text{H}_2$  dissociation along the low-symmetry channels is always larger than along the high-symmetry ones. Similar results have also been obtained for the  $\text{O}_2/\text{Pb}(111)$  system where  $\text{O}_2$  adsorption also prefers the high-symmetry channels<sup>15</sup>. Therefore, we will only discuss the obtained PES cuts along the high-symmetry channels.

From our PES calculations, we find that there are no molecular adsorption states for  $\text{H}_2$  on the  $\gamma\text{-U}(100)$  surface. The calculated 2D PES cuts along the top- $x$ , hol- $d$ , bri- $y$  and bri- $z$  channels are respectively listed in Figs. 3(a)-3(d). The PES cuts along the top- and hol- $z$  channels have similar energy distributions with the bri- $z$  channel, and thus are not listed. Along the other bri- $x$ , top- $x, d$  and hol- $x, d$  adsorption channels, the  $\text{H}_2$  molecule dissociates after overcoming small energy barriers. Only in the PES cut along the hol- $d$  channel, we find a local energy minimum after  $\text{H}_2$  dissociation, which is shown in Fig. 3(b). Along all the other dissociation channels, the H-H bond length is larger than 2.4 Å in the atomic adsorption states after dissociation. So we do not see the local minima in the calculated PES cuts. The local minimum point in Fig. 3(b) corresponds to the adsorption state of two hydrogen atoms in the same surface uranium square hollow. After geometry optimization from this point, we find that the surface uranium atoms are distorted to lower down the free electronic energy. And in the stable adsorption state, the free energy of the adsorption system is 2.59 eV lower than that of an isolated  $\text{H}_2$  molecule plus a clean  $\gamma\text{-U}(100)$  surface.

The most energetically favorable dissociation channel for  $\text{H}_2$  is along the bri- $y$  channel on the  $\gamma\text{-U}(100)$  surface, which is found to be with no energy barriers. As shown in Fig. 3(c), the free electronic energy of the adsorption system drops by about 0.4 eV at the molecular

height of  $h_{\text{H}_2}=0.90$  Å, when the hydrogen bond length  $d_{\text{H-H}}$  becomes 1.90 Å. Our result that  $\text{H}_2$  molecules dissociate without any energy barriers on the  $\gamma\text{-U}(100)$  surface indicates different surface chemical properties of  $\gamma\text{-U}$  with  $\alpha\text{-U}$ , because hydrogen dissociation on the  $\alpha\text{-U}$  surface needs to overcome a small energy barrier of 0.08 eV<sup>19</sup>. And as we will see in the following, the electronic interactions during  $\text{H}_2$  dissociation on the  $\gamma\text{-U}$  surface is different from that on the  $\alpha\text{-U}$  surface.

The PDOS evolution of H and U atoms along the *bri-y* channel is then analyzed to study the electronic interactions during the barrierless dissociation process of  $\text{H}_2$  on the  $\gamma\text{-U}(100)$  surface. We have chosen four points along the minimum energy dissociation path to calculate the PDOS, which are ( $h_{\text{H}_2}=1.17$  Å,  $d_{\text{H-H}}=1.28$  Å), ( $h_{\text{H}_2}=1.02$  Å,  $d_{\text{H-H}}=1.58$  Å), ( $h_{\text{H}_2}=0.90$  Å,  $d_{\text{H-H}}=1.90$  Å), and ( $h_{\text{H}_2}=0.84$  Å,  $d_{\text{H-H}}=2.38$  Å) respectively. The obtained PDOS of the adsorption system at these points are listed in Figs. 4(a)-(d) respectively. As shown in Fig. 4(a), at the molecular height of 1.17 Å, a few electrons transfer from the molecular orbital of  $\text{H}_2$  to the unoccupied *d* states of U, which will be called as the charge donation process at following discussions. At the same time, some electrons also transfer back from U to H, forming a new peak in the hydrogen *s* states near 2.25 eV below the Fermi energy, and we will call it as a charge back-donation process. Since the change in free electronic energy is still negligible at the molecular height of 1.17 Å, as shown in Fig. 3(c), the above electronic hybridizations are not strong.

When the  $\text{H}_2$  molecule further approaches the  $\gamma\text{-U}$  surface, the electronic hybridizations become stronger, and the charge donation and back-donation become more obvious. As shown in Figs. 4(b)-4(d), more and more electrons transfer from *s* states of H to the unoccupied *d* states of U, and more and more electrons transfer from *d* and *f* states of U back to hydrogen. We can also see from Figs. 4(b)-4(d) that the electronic hybridization between H *s* states and U *d* states is always stronger than that with U *f* states. And the charge donation process only happens between H and *d* electronic states of U. Therefore, *d* electronic states of U play very important roles during the dissociation of  $\text{H}_2$  molecules on the  $\gamma\text{-U}$  surface. These results are quite different from the dissociation of  $\text{H}_2$  molecules on the  $\alpha\text{-U}$  surface, where *d* electronic states of U is negligible, and the electronic hybridization happens between hydrogen *s* and uranium *f* electronic states<sup>19</sup>.

To investigate the charge transfer for the dissociative adsorption of  $\text{H}_2$  on the  $\gamma\text{-U}(100)$  surface, we then calculate the atomic charges for the final state of the minimum energy

dissociation path, using the Bader topological method<sup>45</sup>. It is found that after dissociation, the two hydrogen atoms together gain 0.90 electrons, indicating that the ionic part of the H-U bonding plays a significant role during the dissociation process<sup>19</sup>. Different from the dissociation of H<sub>2</sub> on the  $\alpha$ -U(001) surface, where the charge transfer happens only between the topmost U atoms and hydrogen atoms<sup>19</sup>, here we find that the topmost and second atomic layer of the  $\gamma$ -U(100) surface both lose electrons to hydrogen atoms. In comparison with a bare relaxed surface, the topmost and second layer loses 0.58 and 0.34 electrons respectively. This result indicates that the electronic interaction between H<sub>2</sub> and the  $\gamma$ -U(100) surface is not so localized as that between H<sub>2</sub> and the  $\alpha$ -U(100) surface, and also prove the participation of more itinerant *d* electronic states in interactions with hydrogen electrons.

### B. Hydrogen dissociation on the Nb-doped $\gamma$ -U(100) surface

Since the  $\gamma$  phase of U is more stable after doping with 3*d* transition metal atoms. We here also investigate the influences of Nb-doping on the dissociation of H<sub>2</sub> molecules on the  $\gamma$ -U(100) surface. Previous studies have already revealed that doped Nb atoms thermodynamically prefer to substitute U atoms in  $\gamma$ -U, rather than occupy octahedral or tetrahedral vacancies<sup>46</sup>. Thus we only consider the substitutional doping of Nb atoms on the  $\gamma$ -U(100) surface.

Firstly, we do geometry optimization for the Nb-doped U surfaces, with the Nb atom in the topmost, second, and third layer respectively. To simplify our discussions, we will call them as the UNb1, UNb2, and UNb3 surfaces in the following. The relaxed surface structures of the UNb1 and UNb2 surfaces from the top view are shown in Figs. 2(b) and 2(c) respectively. The adsorption sites of H<sub>2</sub> molecules on them are the same as that on the clean  $\gamma$ -U(100) surface as depicted in Fig. 2(a). After geometry optimizations, the uranium atoms in the doping layer are no longer in the same plane with the doped Nb atoms. For example for the UNb1 surface, the *z* coordinate of the Nb atom is 0.16 Å larger than its nearest U atoms, and 0.09 Å smaller than its next neighboring U atoms. The relative surface relaxation of Nb-doped  $\gamma$ -U surfaces can be calculated by averaging the *z* coordinates of the four atoms in the same layer. In this way, the relative relaxation (i.e.,  $\Delta d_{ij}/d_0$  with  $d_{ij}$  and  $d_0$  to be the interval between the *i*th and *j*th atomic layer, and the

lattice interval in bulk  $\gamma$ -U) is calculated and summarized in Table I for the UNb1, UNb2, and UNb3 surfaces. From the results listed in Table I, we can see that the UNb1 surface has much smaller surface relaxations than the clean  $\gamma$ -U(100) surface, indicating that their surface electronic structures are different. As the Nb atom is doped deeper, the surface relaxations tend to approach to the values of undoped  $\gamma$ -U(100) surface.

The PDOS for the UNb1, UNb2, and UNb3 surfaces are also calculated and shown in Figs. 5(b)-5(d), in comparison with the PDOS of the undoped  $\gamma$ -U(100) surface shown in Fig. 5(a). We can see that the electronic states around the Fermi energies are contributed by both the  $d$  electrons of Nb, and  $d$ ,  $f$  electrons of U. Therefore, one can expect that the surface interactions with atoms or molecules should be influenced by the doped Nb atoms, especially for the UNb1 surface where the Nb atom is at the topmost layer. The PES for  $H_2$  on the UNb1 surface is then calculated to study the influences.

The calculated 2D PES cuts for  $H_2$  molecules on the UNb1 surface along the top- $x$ , hol- $d$ , bri- $y$  and bri- $z$  channels are listed in Figs. 6(a)-6(d) respectively. One can see great similarities in the energy distributions with that on the clean  $\gamma$ -U(100) surface. Firstly, along the bri-, top-, and hol- $z$  channels,  $H_2$  molecules can hardly adsorb or dissociate. Secondly, the most energetically favorable dissociation path is along the bri- $y$  channel, which is without any energy barriers. And at last, the  $H_2$  dissociation along the other channels needs to overcome small energy barriers. Nevertheless, because of the introduction of a surface Nb atom, there are also some new features. As shown in Figs. 3(a) and 6(a), the dissociation energy barrier is larger on top of the Nb atom than on top of a U atom of the undoped U surface. And for the most energetically favorable dissociation path, we see that the free electronic energy lowers down much more quickly next to the Nb atom than next to a U atom of the undoped U surface, as shown in Figs. 3(c) and 6(c). These results indicate that the surface electron distribution changes after doping with a Nb atom. The larger energy reduction for  $H_2$  dissociation on the UNb1 surface also suggests that surface doping of Nb atoms reinforces  $H_2$  dissociation, instead of hindering it.

The electronic interactions between  $H_2$  and the UNb1 surface are then studied for the most energetically favorable dissociation channel bri- $y$ . The electronic evolution is analyzed by calculating the PDOS of H and U, Nb atoms at such four points: ( $h_{H_2}=1.50$  Å,  $d_{H-H}=0.84$  Å), ( $h_{H_2}=0.90$  Å,  $d_{H-H}=1.30$  Å), ( $h_{H_2}=0.80$  Å,  $d_{H-H}=1.53$  Å), and ( $h_{H_2}=0.70$  Å,  $d_{H-H}=2.12$  Å) along the dissociation path, which are shown in Figs. 7(a)-7(d) respectively. We can



see from Fig. 7(a) that at the molecular height of 1.50 Å, no obvious electronic interactions happen between H and U, Nb atoms. When the molecular height lowers to be 0.90 Å, some electrons transfer from H<sub>2</sub> to the unoccupied Nb *d* electronic states, corresponding to the charge donation process, and some other electrons transfer back from *d* states of U and Nb to the antibonding orbital of H<sub>2</sub>, corresponding to the charge back-donation process. At the molecular height of 0.80 Å, the charge donation and back-donation processes become more obvious, as shown in Figs. 7(e) and 7(f). We can also see from Fig. 7(e) that the charge donation mainly goes to the *d* orbitals around the Nb atom. In comparison with the electronic interaction between H<sub>2</sub> and the undoped U surface, one can see that the *d* electronic states of Nb largely participate in both the charge donation and back-donation processes. And the stronger electronic hybridizations between hydrogen *s* and Nb *d* states lead to the fact that the free electronic energy lowers down more quickly on the doped  $\gamma$ -U surface.

#### IV. CONCLUSIONS

In conclusion, we have systematically studied the dissociation of H<sub>2</sub> molecules on the clean and Nb-doped  $\gamma$ -U(100) surfaces. We find that both of the two reactions are with no energy barriers. On the clean  $\gamma$ -U(100) surface, there are electronic interactions between hydrogen electrons and U *d* electrons, which cause that H<sub>2</sub> molecules dissociate without any energy barriers along the *bri-y* channel. This mechanism is quite different from the H<sub>2</sub> dissociation on the  $\alpha$ -U surfaces, where *f* electrons of U, instead of *d* electrons take part in the electronic interactions. After surface doping of a Nb atom, we find that not only the H<sub>2</sub> dissociation is with no energy barriers, but also the dissociated hydrogen atoms bond stronger with the surface. The *d* electronic states of Nb participate in the electronic interactions with hydrogen, and causes the larger free energy reduction.

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TABLE I: The relative surface relaxation for the clean  $\gamma$ -U(100) surface, and the UNb1, UNb2, UNb3 surfaces.  $d_{ij}$  represents for the interval between the  $i$ th and  $j$ th atomic layer of each surface, and  $d_0$  is the lattice interval along the [100] direction of bulk  $\gamma$ -U.

surfaces	$\gamma$ -U(100)	UNb1	UNb2	UNb3
$\Delta d_{23}/d_0$	26.4%	17.4%	23.8%	29.9%
$\Delta d_{34}/d_0$	15.6%	7.0%	21.9%	16.0%
$\Delta d_{45}/d_0$	9.8%	0.7%	10.4%	11.1%

## List of captions

**Fig.1** (Color online) The projected density of states for a uranium atom in bulk and in the (100) surface of  $\gamma$ - (a) and  $\alpha$ -U (b). The Fermi energies are set to be zero.

**Fig.2** (Color online) (a) Top view of the clean  $\gamma$ -U(100) surface with the high-symmetry adsorption sites and high-symmetry  $H_2$  orientations depicted. (b) and (c) Top view of the UNb1 [U(100) surface with a doping Nb atom in the topmost layer] and UNb2 [U(100) surface with a doping Nb atom in the second layer] surfaces. (d) Side view of the adsorption model for  $H_2$  on the clean  $\gamma$ -U(100) surface. Blue, grey, and pink balls represent for hydrogen, uranium, and niobium atoms respectively. The adopted supercell is depicted by dashed lines.

**Fig.3** (Color online) The 2D PES cuts for the adsorption of hydrogen molecules along the (a) top- $x$ , (b) hol- $d$ , (c) bri- $y$ , and (d) bri- $z$  channels on the clean  $\gamma$ -U(100) surface. The total energy of a free  $H_2$  molecule plus that of the  $\gamma$ -U(100) surface is set to be the energy zero.

**Fig.4** (Color online) The projected density of states for the  $H_2/\gamma$ -U(100) adsorption system along the energetically most favorable dissociation path with the height of  $H_2$  center of mass to be 1.17 Å (a), 1.02 Å (b), 0.90 Å (c), and 0.84 Å (d). The Fermi energies are all set to be zero. (e) and (f) The partial charge density distributions for the two energy peaks denoted in (c). Blue and grey balls represent for hydrogen and uranium atoms respectively. The yellow dots represents for the isosurface of partial charge density.

**Fig.5** (Color online) (a) The projected density of states for the clean  $\gamma$ -U(100) surface. (b), (c), and (d) The projected density of states for the Nb doped  $\gamma$ -U(100) surface, with the Nb atom at the topmost, second, and third layer. The Fermi energies are all set to be zero.

**Fig.6** (Color online) The 2D PES cuts for the adsorption of hydrogen molecules along the (a) top- $x$ , (b) hol- $d$ , (c) bri- $y$ , and (d) bri- $z$  channels on the UNb1 surface. The total energy of a free  $H_2$  molecule plus that of the Nb doped  $\gamma$ -U(100) surface is set to be the energy zero.

**Fig.7** (Color online) The projected density of states for the adsorption system of  $\text{H}_2$  on the Nb-doped  $\gamma\text{-U}(100)$  surface, along the energetically most favorable dissociation path with the height of  $\text{H}_2$  center of mass to be 1.50 Å (a), 0.90 Å (b), 0.80 Å (c), and 0.70 Å (d). The Fermi energies are all set to be zero. (e) and (f) The partial charge density distributions for the two energy peaks denoted in (c). Blue, grey, and pink balls represent for hydrogen, uranium, and niobium atoms respectively. The yellow dots represents for the isosurface of partial charge density.

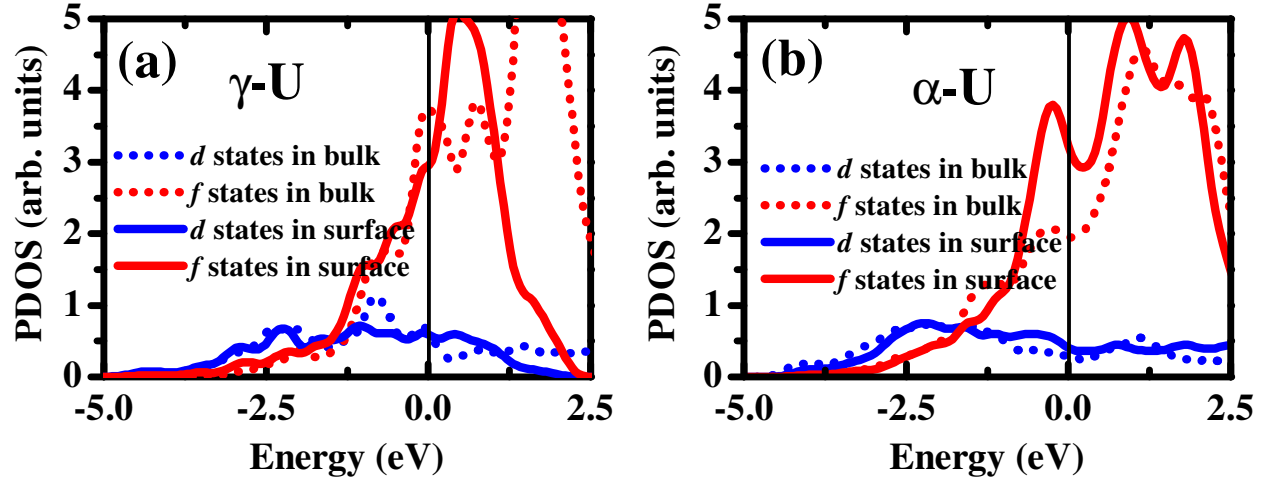


FIG. 1:

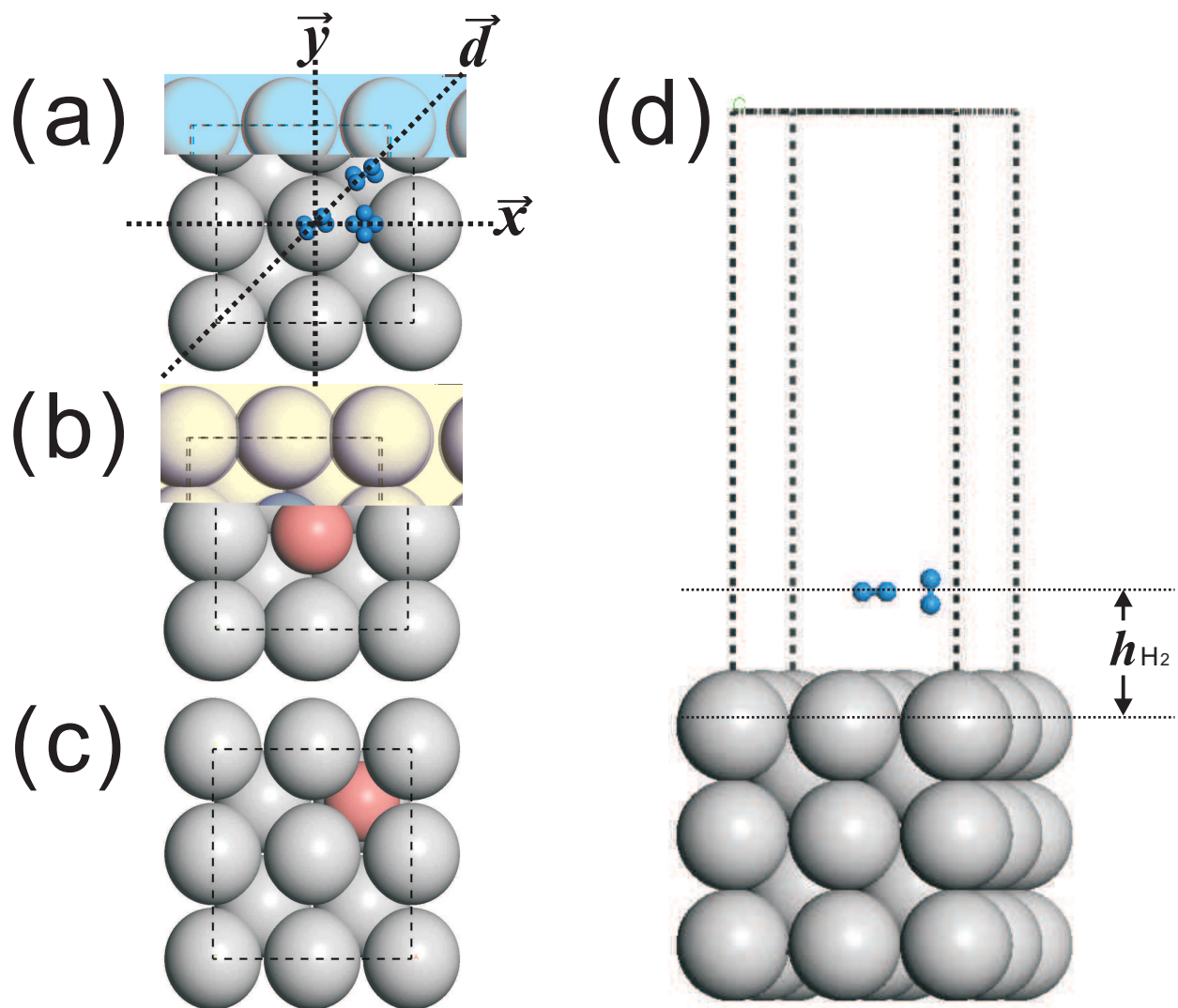


FIG. 2:



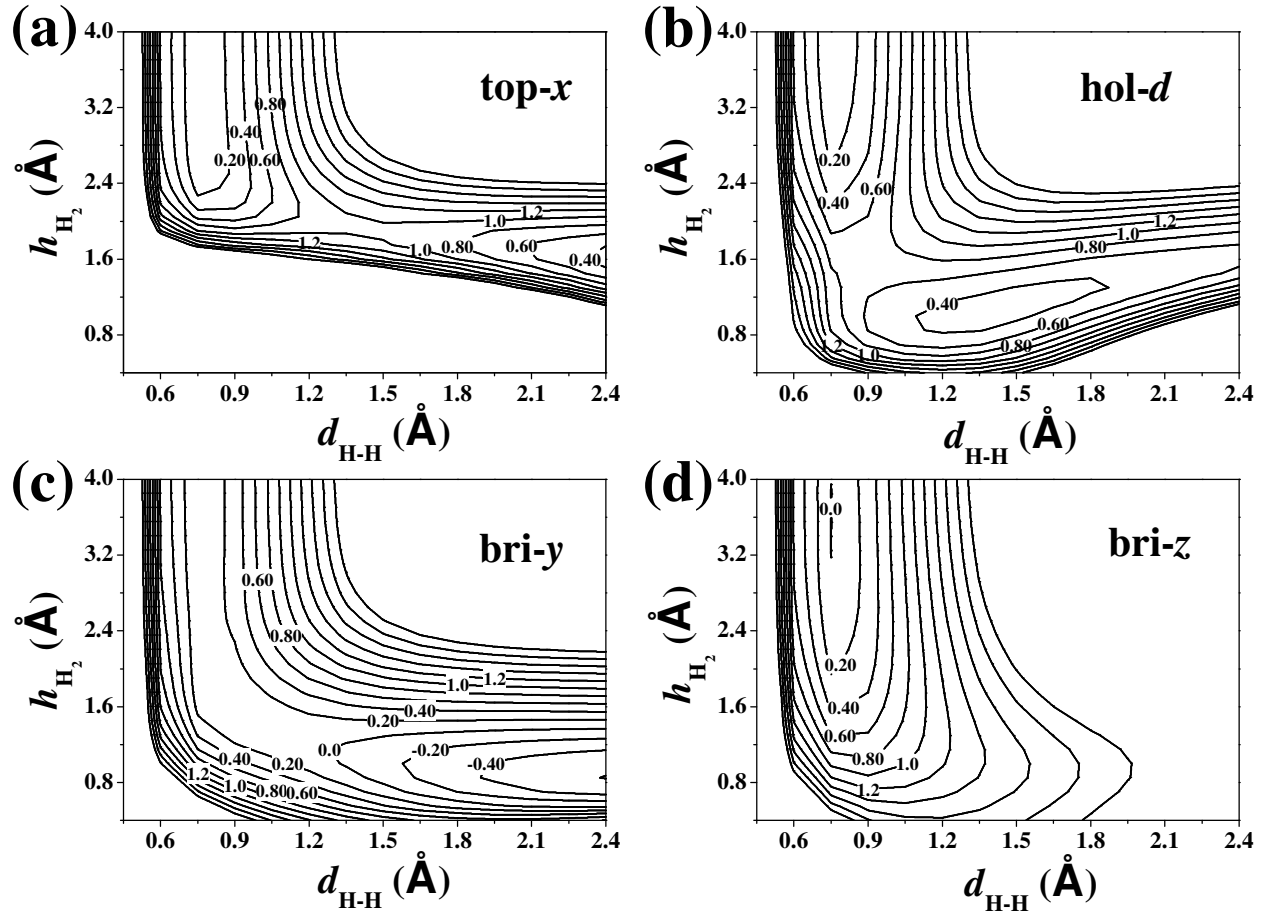


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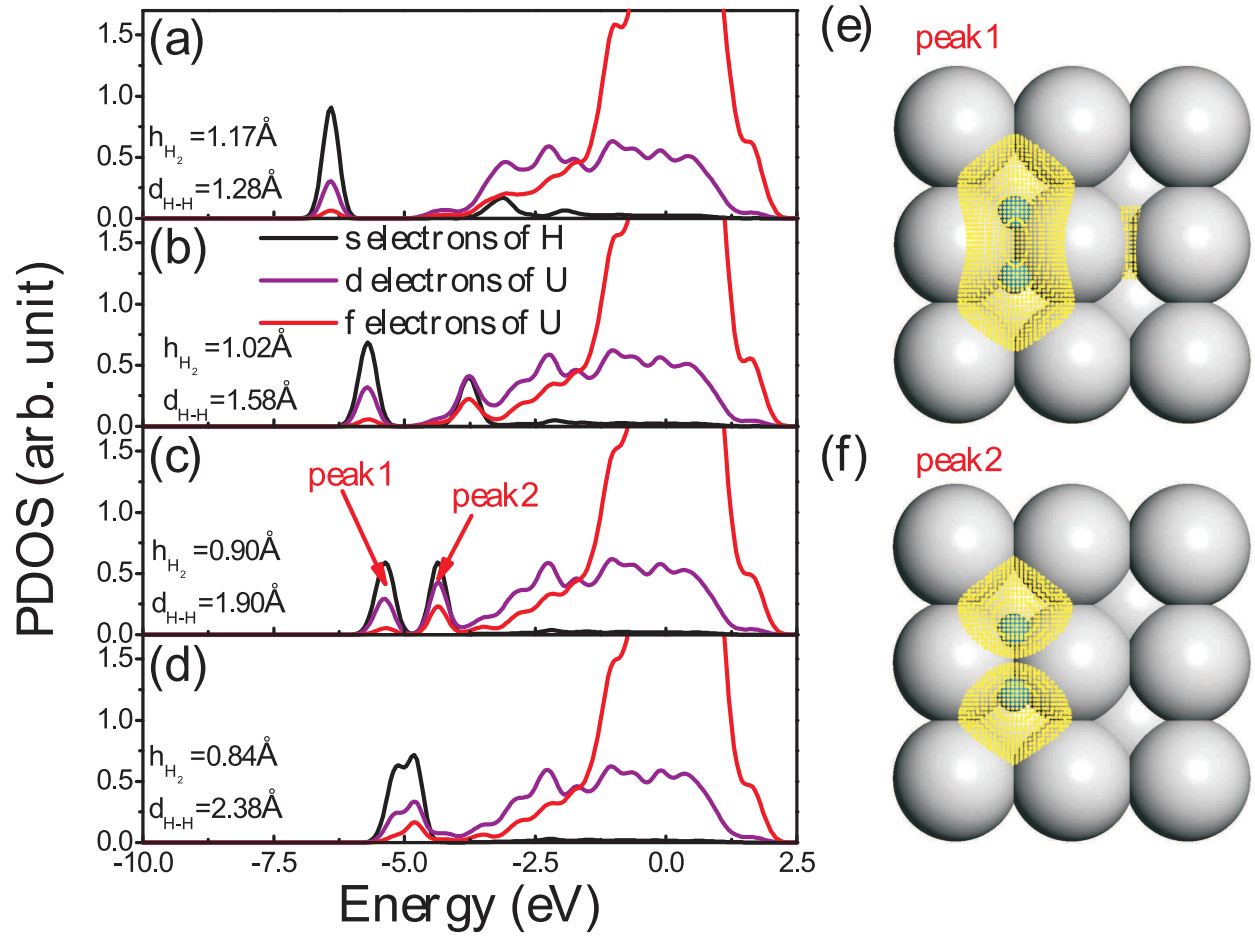


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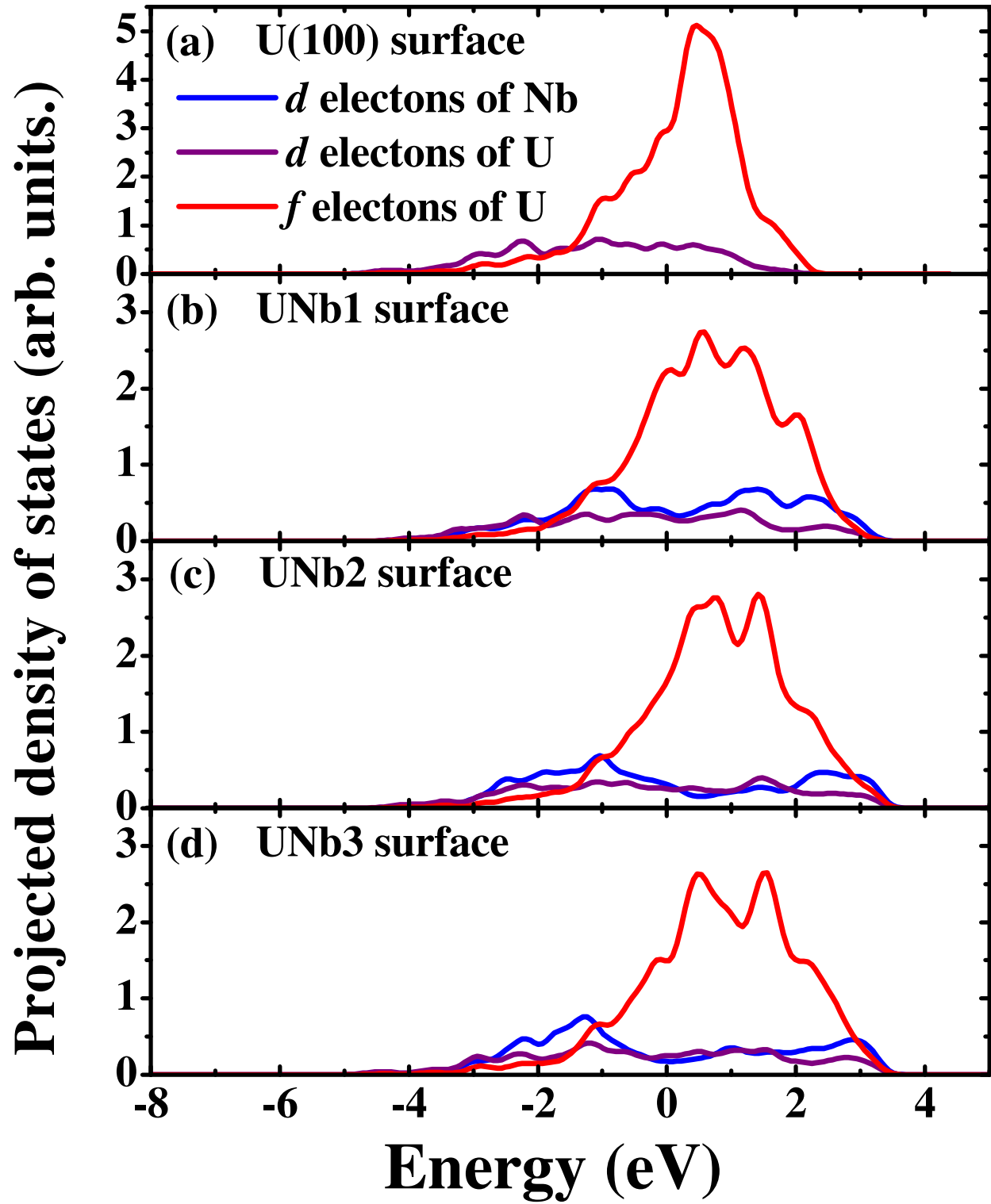


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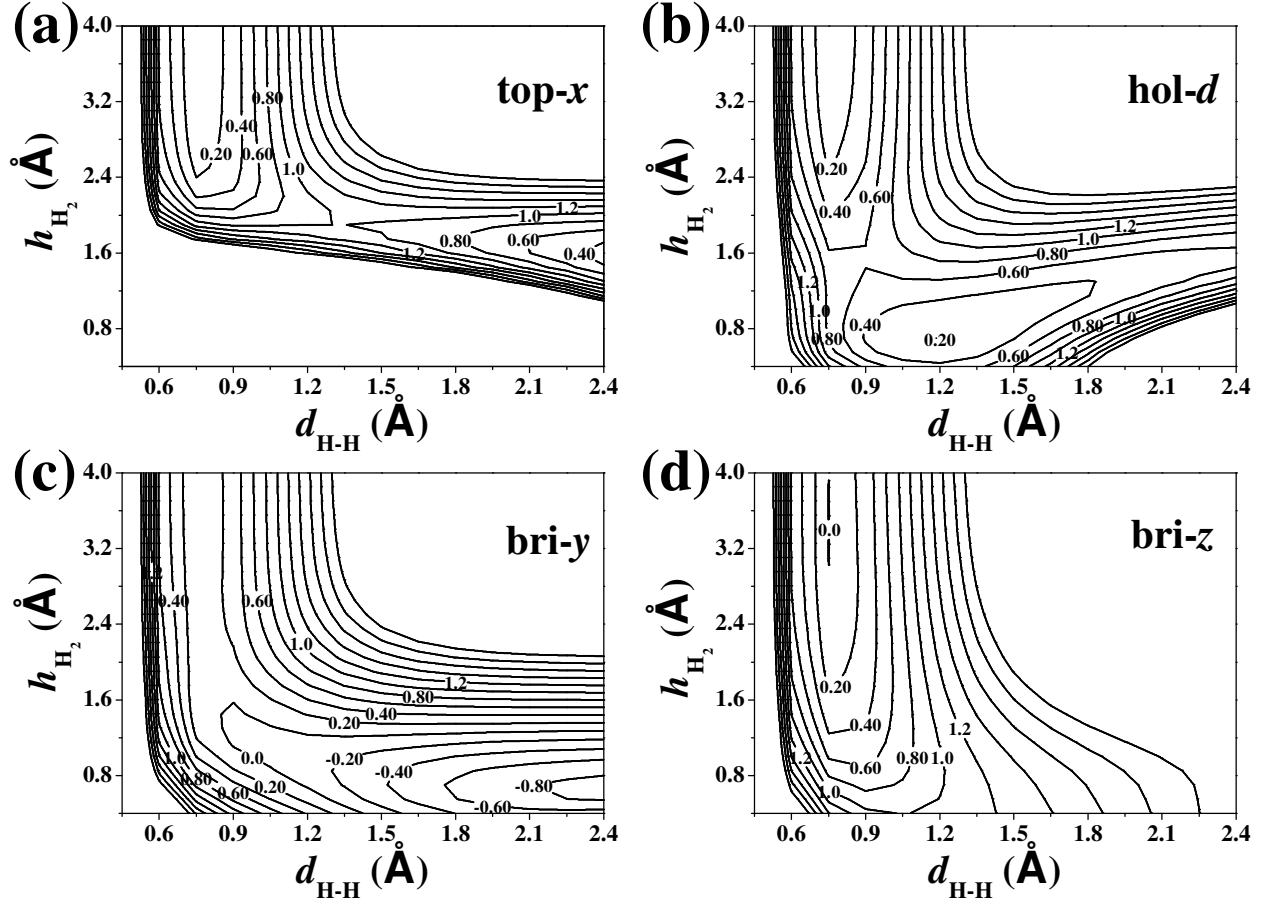


FIG. 6:

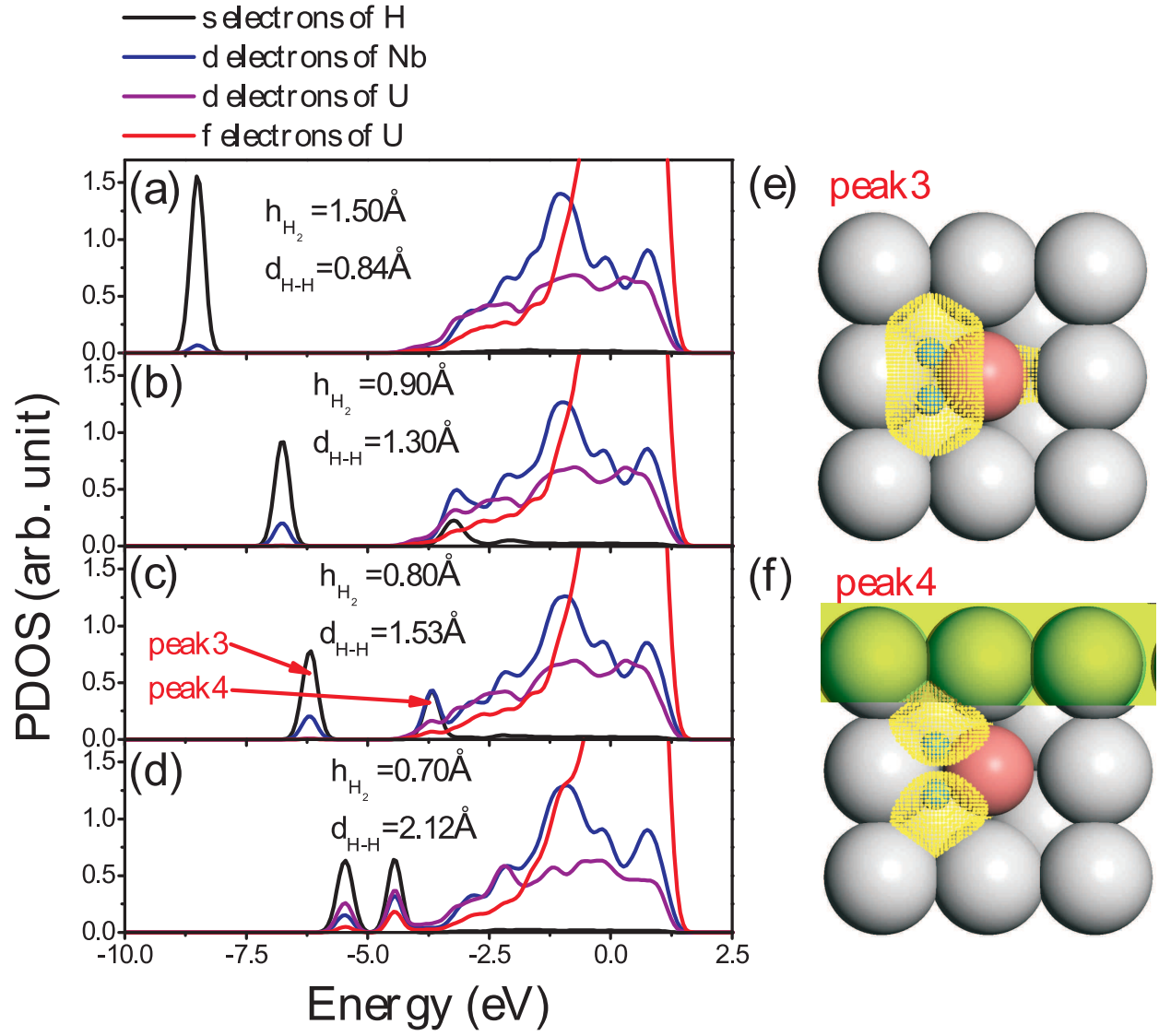


FIG. 7: